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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of :
 Toshiro NISHI, et al. : Group Art Unit: 1745
 Serial Number: 09/118,833 : Examiner: CREPEAU. J
 Filed: 07.20.1998 :
 For: SOLID ELECTROLYTE TYPE FUEL BATTERY

Declaration under 37 CFR 1.132

I. I, Toshiro NISHI, declare

1. That I am the same person who executed the Declaration filed in the patent of the above-identified application;
 that I have been employed by MITSUBISHI HEAVY INDUSTRIES, Ltd. for 18 years and 10 months, and have worked at the Research Laboratory of the Company.
2. That I have conducted experiments in order to demonstrate unexpected effects of the invention described in United States Patent Application Serial No. 118,833 over compositions described in the cited U.S. Patent issued to SOMA et al.
3. That I have performed or supervised the performance of the experiments described below and have reviewed the results thereof as reported below.
4. That the conclusions stated herein are based upon this review of the results and my experience in this

field.

5. Toshiro NISHI, the declarant, has been involved in research into fuel batteries in the Research Laboratory of the Company for 17 years. He and his colleagues, Nobuaki MURAKAMI and Hirokazu YAMAMOTO, found a process to reduce the cost for producing fuel batteries and to simplify the production process by using an interconnector comprised of a specific composition, and applied for U.S. Patent in July 20, 1998.

In order to substantiate the difference from the cited patent issued to Soma et al., we hereby submit with tests results described below.

6. Tests

- (1) Fuel Battery prepared by Sintering Process (Present invention)

As the material, MTiO_3 , which is concretely $\text{Ca}_{0.9}\text{La}_{0.1}\text{TiO}_3$ as described in the claim 4 of the present invention, is used.

The detail procedure is accorded with the procedure described in Appendix A-1 attached herewith, "Evaluation of Interconnector Preparation Method of Interconnector", and Appendix A-2 attached herewith, "Performance of Sintered Cells and Module Manufacturing Process of Sintered Cell".

These references are parts of papers prepared on June, 1998 by the declarant for their lecture regarding fuel batteries prepared by employing Sintering process.

Namely, as written in the Appendix A-1, CaCO_3 , TiO_2 and La_2O_3 are incorporated and mixed by using a ball mill, and the mixture was then subjected to firing.

Then, as shown in the Appendix A-2, the slurry is printed in band pattern by means of screen printing method around the surface of the substrate 11 being prepared by extrusion molding.

At this stage, as shown in Fig. 44 in the description in the present patent application, a material for a fuel electrode 12 is laminated onto the side surface of the base tube 11, and a material for an electrolyte 13 and a material for an interconnector 14 are then laminated onto the fuel electrode in series, and the laminated materials were subjected to the first sintering process at approximately $1,300^\circ\text{C}$. Then, the slurry for an air electrode is printed in band pattern and is then subjected to the second sintering process at $1,250^\circ\text{C}$ to obtain the cell.

(2) Fuel Battery prepared by Thermal Spraying Process

In this process, LaCrO_3 is used as the material.

More specifically, hybrid plasma spraying torch, which is described in Fig. 2 in the Appendix B, is used and the condition for the thermal spraying is accorded with that shown in the Table 2.

The temperature employed for the thermal spraying was 2000°C .

When employing the thermal spraying process, it requires very laborious steps, i.e., thermally spraying a material

for a fuel electrode onto a substrate 11 to form a fuel electrode 12, then applying masking and thermally spraying a material for an electrolyte to form an electrolyte 13, then applying masking and thermally spraying a material for an interconnector to form an interconnector 14, and finally applying masking and thermally spraying a material for an air electrode to obtain an air electrode 15.

(3) The following is a comparative difference in between the fuel battery prepared by sintering process and thermal spraying process.

	Fuel Cell prepared by Thermal Spraying Process	Fuel Cell prepared by Sintering Process (Present Invention)
Required time for Production	150 min/fuel cell	15 min/fuel cell
Yield on materials	3 - 10%	90% or more
Equipment cost	Basic amount	1/10
Construction cost	Basic amount	1/5
Materials cost	Basic amount	1/2
Cell production cost	1.3 million yen/kw	50,000 yen/kw

As shown above, the sintering process of the present invention can markedly decrease the production cost in comparison with the thermal spraying process of the citation. This is neither disclosed nor suggested in the citation SOMA et al .

In particular, in case of the thermal spraying process, the yield on materials is very low since most of the materials are consumed as useless during the thermal spraying. While in case of the sintering process according to the present invention, the yield on materials is improved as much as

10-30 times comparing to the thermal spraying process, which contributes to greatly decrease the materials cost.

Furthermore, in the thermal spraying process described above, no heat treatment at 1,250°C or higher is applied following to the thermal spraying as done in the citation of Soma et al., and therefore, the equipment cost for applying heat treatment must be further required and more time will be required for the production in case of employing the thermal spraying process.

In addition, according to the present invention, an advantageous effect of improved impaction property can be attained based on strong bonding force given by the chemical co-sinter in which oxygen (O) is shared.

On the other hand, in case of the thermal spraying process, the materials tend to be easily exfoliated because the bonding is provided in a form of weak intermolecular force such as static electricity.

This advantageous characteristic provided by the present invention is an essential feature to be used as a fuel cell which is required to be used over a long time.

Accordingly, the material for the interconnector in a fuel cell prepared by the thermal spraying process, which is remarkably different from the production process in the present invention, cannot necessarily be directly used for the interconnector in a fuel cell prepared by the sintering process. That is, the fact that MtiO_3 , which is expressed

as $\text{Ca}_{0.9}\text{La}_{0.1}\text{TiO}_3$ in the present declaration letter, is suitable for the material to be used for an interconnector in a sinter type fuel cell was found for the first time by the inventors of the present invention.

II. The undersigned further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and, further, that these statements were made with knowledge that willful, false statements, and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of title 18 of the United State Code and that such willful, false statements may jeopardize the validity of the above-identified application or any patent issuing thereon.

Toshiro Nishi

Toshiro Nishi

Dated: This 2nd day of February, 2001

Appendix:

Appendix A-1

Appendix A-2

Appendix B

EVALUATION of Interconnector Preparation Method of Interconnector

MO or MCO₃

(CaCO₃ etc.)

TiO₂

Ln₂O₃

(La₂O₃ etc.)

Mixing (Ball Mill, 24h)

Calcination (1473K×5h)

Grinding (Ball Mill, 48h)

Forming (CIP, 200MPa)

Sintering

Characterization

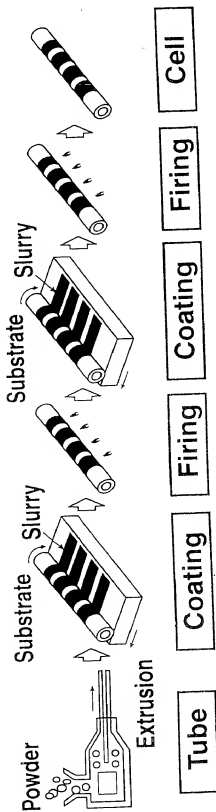


Manufacturing of
Sintered Cell
(Next page)



MITSUBISHI
HEAVY INDUSTRIES, LTD.

PERFORMANCE of Sintered Cells and Module Manufacturing Process of Sintered Cell



POINT

- ① High Yield
- ② Non Masking
- ③ Simple Facilities

EFFECT

- ↑ Reduction of Material Cost
- ↑ Reduction of Process
- ↑ Reduction of Equipment Investment

STUDY ON R.F. PLASMA SPRAYING

- A Newly Developed Process of Plasma Spraying -

Akira Notomi*, Yasuyuki Takeda*, Masaru Kodama* and Masayoshi Shitamichi*

ABSTRACT

A new plasma spraying process has been developed, which utilizes a radio frequency induced plasma or a hybrid plasma of r.f. and d.c. arc plasma. The r.f. plasma has a wider controlling range of plasma than that of the conventional d.c. arc plasma. The r.f. plasma and hybrid plasma spraying of ZrO_2 and $LaCrO_3$ particles were studied, stabilizing the plasma condition. It is indicated that this new plasma spraying process has a potential to produce a dense coating of ceramics.

1. INTRODUCTION

Thermal spraying has been applied in a wide range for wear, corrosion and heat resistant coatings. Especially in thermal spraying processes, d.c. arc plasma (d.c. plasma) spraying is the most promising one, which is able to produce the coatings of refractory metals and ceramics because of its high temperature plasma. However, the high temperature region of d.c. plasma is so narrow and gas velocity is so high that there would be many unmelted particles in the coating. This could cause to decrease the adhesive, cohesive strength and density of coating.

On the other hand, radio frequency plasma (r.f. plasma) has wide high temperature region of several cm diameter, and low gas velocity, which could melt the spraying particles sufficiently¹⁾. Hybrid plasma of r.f. and d.c. plasma could widen a plasma controlling range and is considered to have potential to produce a denser coating of new material which have been difficult to produce by conventional process²⁾.

In this study, r.f. plasma torch and hybrid plasma torch were trially manufactured and the stabilizing conditions of plasma generation were obtained. Using these plasma torches, plasma spraying of ceramics was carried out, by which result it is confirmed that these new plasma processes could produce a denser and functional coatings.

* Nagasaki R & D Center, Mitsubishi Heavy Industries, Ltd. Japan

2. EXPERIMENTAL PROCEDURE

Fig. 1 shows a trially manufactured r.f. plasma torch. A water cooled quartz tube of inner diameter 57 mm is set in r.f. coil of 3 turns. Sheath gas and carrier gas flow into the quartz tube from gas nozzle which located in upper side of quartz tube. Sheath gas has two flows of radial and tangential direction which effect on stabilizing a plasma and cooling a quartz tube. Particles can be supplied into quartz tube throughout center of gas nozzle by carrier gas.

Fig. 2 shows a trially manufactured hybrid plasma torch where d.c. plasma torch is set on the upper side of quartz tube in place of gas nozzle used in r.f. plasma torch. Sheath gas of radial direction flows into the quartz tube. Particles are supplied to the tip of d.c. plasma torch.

Input power and frequency of r.f. generator used are 130 KVA max., 4 MHz respectively. Commercial d.c. plasma torch of input power 30 KVA, nozzle diameter 5 mm is used for hybrid plasma torch. It is important to know the operating conditions to stabilize a plasma because of absence of electrode in r.f. plasma torch. The appropriate conditions of gas flow rate and input power are studied concerning with both of r.f. and hybrid plasma. $ZrO_2-12wt\%Y_2O_3$ (YSZ) particles (30~50 μm) were r.f. plasma sprayed on the substrate varying the distance from torch. The diameters of flattened particles were measured. $LaCrO_3$ particles (20~85 μm) were also r.f. and hybrid plasma sprayed on the substrate, and the coatings were compared with d.c. plasma sprayed one.

3. RESULTS AND DISCUSSION

Fig. 3 shows the r.f. plasma operating conditions to maintain a stabilized plasma concerning with the relation between r.f. input power and H_2 flow rate as secondary gas which is supplied to sheath gas of radial direction. Fig. 4 also shows the hybrid plasma operating condition concerning with the relation between r.f. input power and d.c. input power.

Based on Fig. 3, r.f. plasma spraying conditions were determined as shown in Table 1. Fig. 5 shows the relation between flattened particle diameter and ratio of particle number as parameter of distance from torch to substrate. There is maximum ratio of particle number at the diameter of 70~90 μm (flattened ratio: 1.5~2.0) independently of the distance from torch to substrate. The maximum value of the ratio of particle number is obtained at $d=45$ mm. Fig. 6 shows SEM photographs of the surface of YSZ coating by the above conditions. There can be seen widely flattened particles in r.f. plasma sprayed coating, while the flattened ratio is not so high in the conventional d.c. plasma sprayed coating. However, the adhesive strength of particles in r.f. plasma sprayed coating is lower than that of

the latter one, which is considered that the kinetic energy of particles in r.f. plasma is not sufficient for dense coating of ceramics.

Hybrid plasma would have a potential to be an effective process to solve this problem. Hybrid plasma spraying of LaCrO_3 was carried out using the spraying conditions as shown in Table 2. The r.f. and d.c. plasma spraying were also carried out to compare with that. Fig. 7 shows SEM photographs of surfaces and fracture surfaces of the coatings by three processes. Hybrid plasma sprayed coating shows the highest flattened ratio of particle and seems to be the densest one from fracture surface. There also can be seen flattened particles in r.f. plasma coating, of which flattened ratio is not so high. The flattened particles and dispersed fine particles are observed on the surface of d.c. plasma sprayed coating, of which fracture surface does not show a dense structure. These results show that hybrid plasma spraying could produce a denser ceramic coating than the other plasma spraying process.

It should be necessary to take into account of characteristics of spraying material and coating function needed, in applying r.f. plasma or hybrid plasma spraying process effectively.

4. CONCLUSIONS

The r.f. plasma and hybrid plasma spraying of ceramics which have wide controlling range of plasma were carried out as new plasma spraying processes. The results obtained were summarized as follows:

- (1) The r.f. plasma sprayed particles of $\text{ZrO}_2\text{-12wt\%Y}_2\text{O}_3$ were sufficiently flattened on the surface of substrate, which would show possibility to produce a dense ceramic coating. However, the adhesive strength of particles was not so good under the spraying conditions used.
- (2) Hybrid plasma spraying of LaCrO_3 produces denser coating than r.f. and d.c. plasma spraying process, which would show that hybrid plasma spraying process has potential to produce dense coating of high melting point material and ceramics.

REFERENCES

- 1) S. Takeuchi, T. Okada, T. Yoshida and K. Akashi: J. Japan Inst. Metals, 52, 711 (1988).
- 2) T. Okada, H. Hamatani and T. Yoshida: J. Am. Ceram. Soc. 72[11] 2111-16 (1989).

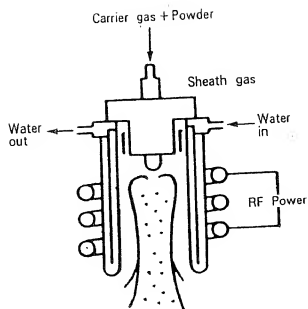


Fig.1 R.F. plasma spraying torch

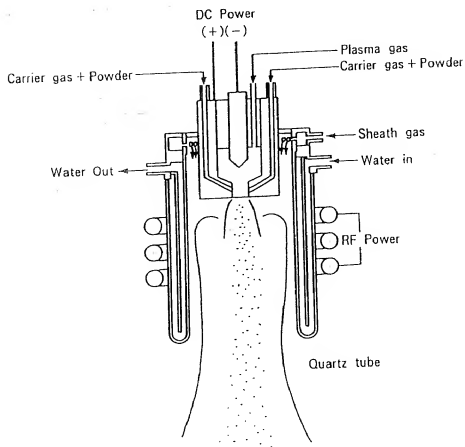


Fig.2 Hybrid plasma spraying torch

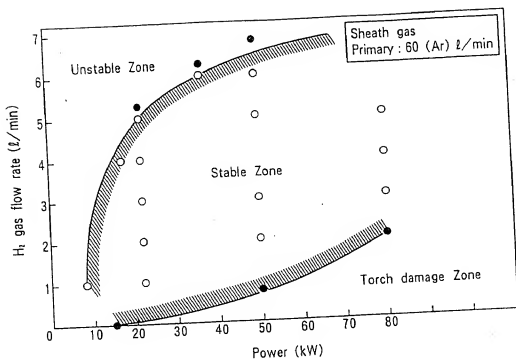


Fig.3 Effect of secondary gas (H_2) flow rate on stability of R.F. plasma

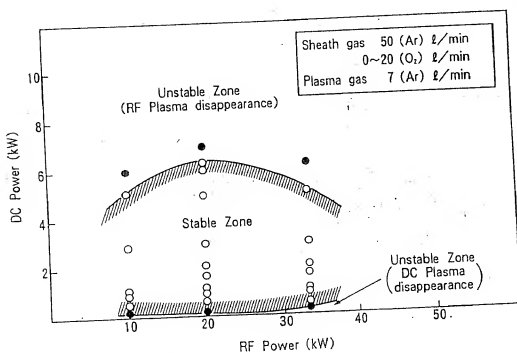


Fig.4 Effect of R.F. and D.C. power on stability of hybrid plasma

Table 1 Conditions of R.F. plasma spraying

Material	Size (μm)	RF Plate Power (kW)	Sheath gas (ℓ/min)	Carrier gas (ℓ/min)	Powder feed (g/min)	Spraying Distance (mm)
ZrO_2 -15(wt) Y_2O_3	30~50	50	50 (Ar) 5 (H_2)	9 (Ar)	10	5~45

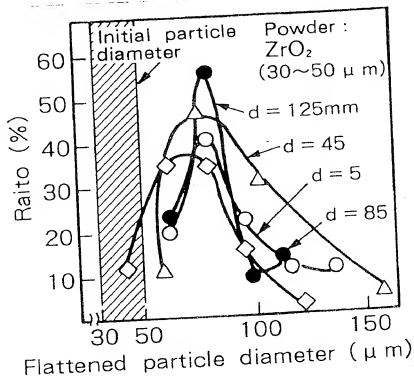
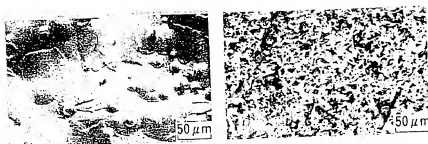


Fig.5 Distribution of flattened ratio of R.F. plasma sprayed particles



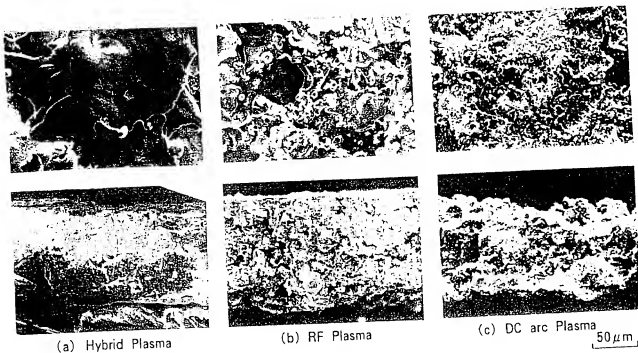
(a) RF Plasma

(b) DC arc Plasma

Fig.6 Surface microstructures of R.F. and D.C. plasma sprayed coatings of YSZ

Table 2 Conditions of hybrid plasma spraying

Material	Size (μm)	Power (kW)		Gas flow rate (l/min)			Powder feed (g/min)	Spraying distance (mm)
		RF Plate	DC	Sheath gas	Plasma gas	Carrier gas		
LaCrO ₃	20~85	20	7	50 (Ar)	5 (Ar)	3.5 (Ar)	1	10



(a) Hybrid Plasma

(b) RF Plasma

(c) DC arc Plasma

Fig.7 Surface and fracture surface microstructures of plasma sprayed coatings of LaCrO₃

PATENT
0965-0232P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicants: Toshiro NISHI et al. Conf.: 9403
Serial No.: 09/118,833 Art Unit: 1745
Filed: July 20, 1998 Examiner: J. CREPEAU
For: SOLID ELECTROLYTE TYPE FUEL BATTERY

DECLARATION UNDER 37 C.F.R. §1.132

Assistant Commissioner for Patents
Washington, DC 20231

Sir:

I, Toshiro NISHI, do declare and say as follows:

1. I am one of the inventors of the U.S. Patent Application Serial No. 09/118,833, filed July 20, 1998, and I am familiar with the contents of the application, its prosecution before the U.S. Patent and Trademark Office, and the references cited therein. I am a citizen of Japan, residing at c/o Nagasaki Research & Development Center, Mitsubishi Heavy Industries, Ltd., 717-1, Fukahori-machi 5-chome, Nagasaki-shi, Nagasaki, Japan. I have been employed by Mitsubishi Heavy Industries, Ltd. for over 20 years, and have worked at the Research Laboratory of the Company.

2. I have studied the contents of U.S. Patent 5,411,767, hereinafter referred to as SOMA.

3. To show the superiority of the present invention, I am submitting the attached SEM photomicrographs of plasma sprayed material (A) and co-sintered material (B). In reference to these SEM photomicrographs (A) and (B), I am making the following observations:

When plasma spraying is applied as in SOMA and other conventional art processes, a number of air spaces are produced in the plasma-sprayed film having a thickness of from several to dozens of microns. This can be clearly observed in the dense-blue cored portion of SEM photomicrograph (A) (also note the micron bar for scale).

In contrast, when the inventive co-sintering is utilized, a film having a very dense structure is formed. This is clearly observable in SEM photomicrograph (B). Incidentally, the portions that appear to be air spaces in SEM photomicrograph (B) are produced during thermal etching. However, the sizes of these air spaces are very small, on the order of submicrons, as indicated by the micron bar for scale.

As a result, a "sintered" or "co-sintered" material such as an interconnector does not represent a process step. Instead, a "sintered" or "co-sintered" material represents a physical state of matter that is achieved through the sintering process. This state of matter is readily discernable by comparing SEM photomicrographs (A) and (B).

Therefore, the plasma sprayed film of SOMA is incapable of attaining the sintered or co-sintered interconnector of the invention. Therefore, SOMA fails to either teach or suggest a sintered or co-sintered interconnector of the invention. The high density achievable by the inventive technology and demonstrated in the attached SEM photomicrographs are a clear demonstration of unexpected results over SOMA.

4. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

October 29, 2002
Date

By Toshiro Nishi
Toshiro NISHI

PATENT
0965-0232P

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When plasma spraying is applied as in SOMA and other conventional art processes, a number of air spaces are produced in the plasma-sprayed film having a thickness of from several to dozens of microns. This can be clearly observed in the dense-blue cored portion of SEM photomicrograph (A) (also note the micron bar for scale).

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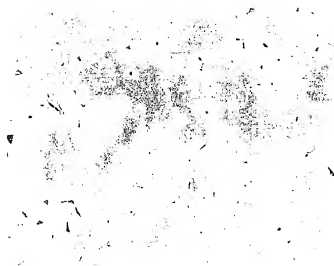
January 27, 2003
Date

By Toshiro Nishi
Toshiro NISHI



100 μm

(A)



(B)